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by George M. Prok

Lewis Research Center

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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# TWO-STEP PROCESS TO INCREASE ATOMIC HYDROGEN ION PRODUCTION IN LOW-PRESSURE RADIOFREQUENCY DISCHARGE

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## SUMMARY

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Atomic ion production in a low-pressure hydrogen plasma was improved by employing a two-step process. In the first step, hydrogen molecules are dissociated at high pressures (approximately  $450\mu$ ) with microwaves at a frequency of 2450 megacycles. The second step consists of expanding the partially dissociated hydrogen through an orifice to the low-pressure region (3 to  $6\mu$ ), where it is ionized by a radiofrequency coil, which is operated at a frequency of 14 megacycles. Atomic hydrogen decay in the low-pressure region was minimized by eliminating all catalytic surfaces. The maximum increase in proton production was found to be 300 percent above that of a hydrogen plasma with no predissociation. This maximum improvement occurred when the low-pressure region was at 3.2 microns. The intensities of the  $H_{\eta}$ ,  $H_{\theta}$ ,  $H_{\epsilon}$ , and  $H_{\kappa}$  Balmer lines, which were determined experimentally to have essentially no molecular contribution, were used to determine the increase in atomic hydrogen ion-production rate over that of no prior dissociation.

*Author*

## INTRODUCTION

The production of a hydrogen plasma with an atomic hydrogen ion density above  $10^{12}$  per cubic centimeter is important to the ion cyclotron resonance heating experiments currently in progress at the Lewis Research Center (ref. 1). In these experiments, atomic hydrogen ions at low pressures ( $2\mu$ ) are selectively heated by ion cyclotron waves that are generated by a suitably designed radiofrequency coil. In their discussion on hydrogen, Massey and Burhop point out that proton production is a function of the hydrogen atom concentration (ref. 2). Other investigators who have studied hydrogen plasmas have also shown that as the atomic hydrogen concentration increases the production rate

of atomic hydrogen ions increases (refs. 3 and 4). Since a high hydrogen atom concentration is important for proton production, dissociation by processes within the plasma or by some external means should be advantageous.

Hydrogen dissociation and free radical research shows that, at high pressures (80 to 500 $\mu$ ), 90-percent dissociation can be obtained with microwaves, but at pressures below 10 microns less than 10 percent of the gas is dissociated (refs. 5 to 7). The ion cyclotron resonance experiments are done at pressures of about 2 microns or less; therefore, external means such as predissociation are required for increasing the atomic hydrogen concentration. The effectiveness of increasing the atomic hydrogen ion-production rate by predissociation is not theoretically predictable because of competing processes involving dissociation, gas-phase recombination, surface recombination, and surface adsorption (refs. 8 to 12). Hence, the purpose of the present study was to evaluate experimentally the effectiveness of predissociation.

A technique where hydrogen is dissociated by a separate source before ionization would make the atom concentration a controlled variable. In addition to being useful to ion cyclotron resonance heating, such a technique would be useful for experimentally determining the radiation loss contributed by each of the species in a hydrogen plasma. The work reported herein could also be useful in the determination of excitation functions for atomic hydrogen, where low-pressure plasmas are required (ref. 13).

## THEORY

The reaction



is the dominant process for proton production in a hydrogen plasma (ref. 3). The volume production rate of  $H^+$  from the reaction in equation (1) is given by

$$\dot{N}_{H^+} = N_H N_e \langle \sigma_{H^+}(V_e) V_e \rangle \quad (2)$$

where

$\dot{N}_{H^+}$	volume production rate of $H^+$
$N_H$	atomic hydrogen density
$N_e$	electron density

$\sigma_{H^+}(V_e)$  excitation function for ionizing hydrogen atoms  
 $V_e$  electron velocity

The relation between line intensity of a transition and atom concentration for lines which have no contribution from molecular excitation is (ref. 14)

$$I_{jk} = N_H N_e \langle \sigma_j(V_e) V_e \rangle P_{jk} \quad (3)$$

where

$I_{jk}$  intensity of a j to k transition  
 $\sigma_j(V_e)$  excitation cross section to state j  
 $P_{jk}$  transition probability for j to k transition

Combining equations (2) and (3) yields

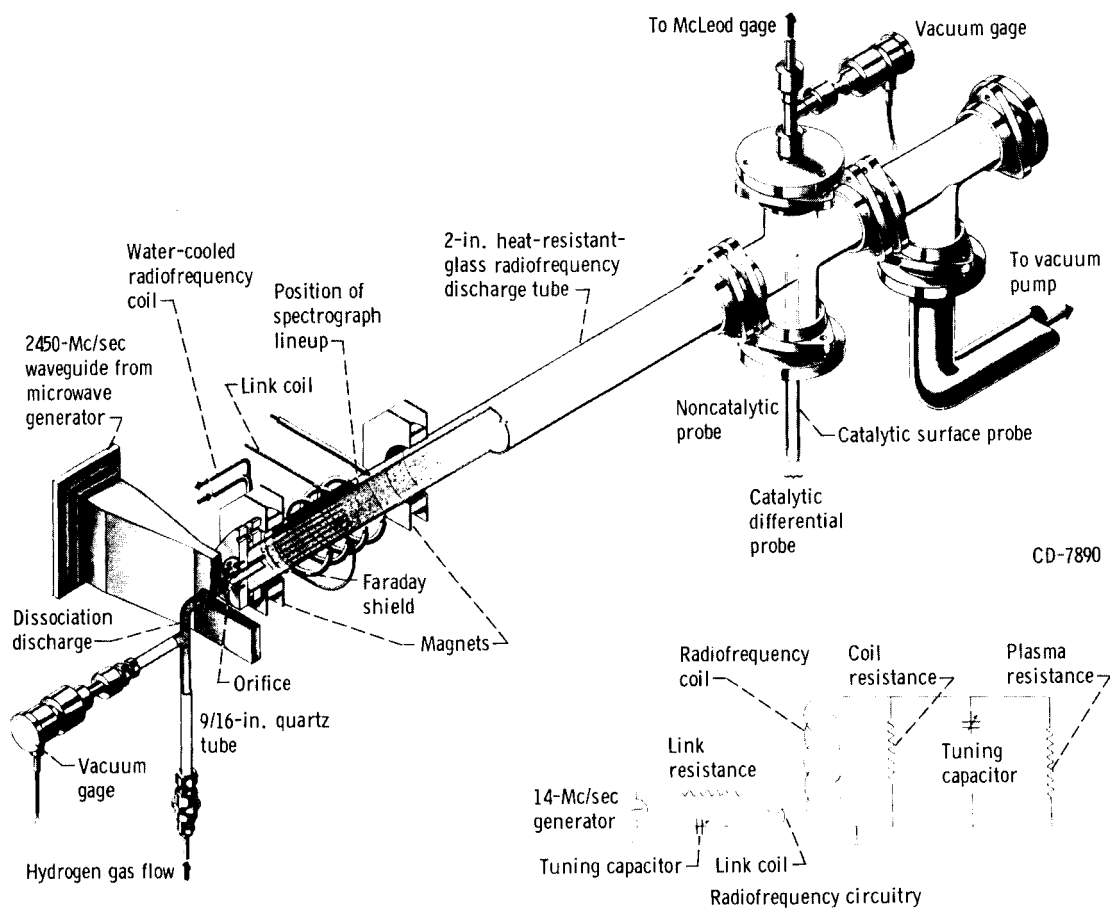
$$I_{jk} = \frac{\langle \sigma_j(V_e) V_e \rangle P_{jk}}{\langle \sigma_{H^+}(V_e) V_e \rangle} \dot{N}_{H^+} \quad (4)$$

If the electron energy distribution remains constant, equations (3) and (4) indicate that  $I_{jk}$  is directly proportional to  $\dot{N}_{H^+}$ . If the electron density is also constant,  $\dot{N}_{H^+}$  is proportional to  $N_H$  as shown by equation (2). Hence, for two different atom concentrations  $N_H$  and  $N_H'$ , the ratio may be written

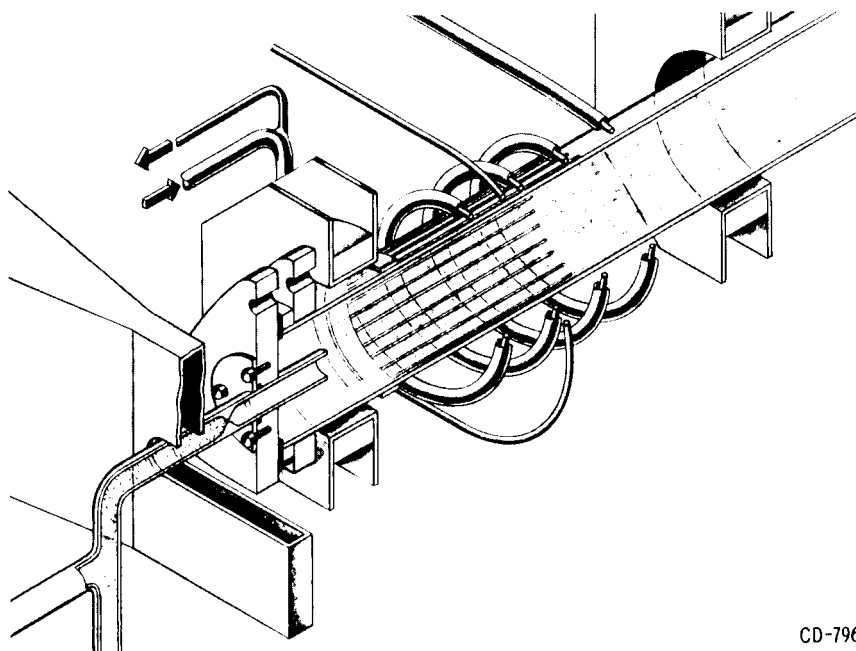
$$\frac{I_{jk}}{I'_{jk}} = \frac{N_H}{N_H'} \quad (5)$$

## APPARATUS

A drawing of the apparatus is shown in figure 1(a). Figure 1(b) is an enlarged view of the orifice section. Hydrogen gas was dissociated in the part of the tube that was inserted in the slot of the microwave cavity. The microwave generator was operated at 2450 megacycles per second. The low-pressure plasma was produced by a radiofrequency coil operated at 14 megacycles per second. The apparatus and the technique for pre-dissociation were optimized according to requirements reported in reference 5. These



(a) Overall view.



(b) Enlarged view of orifice section.

Figure 1. - Experimental apparatus.

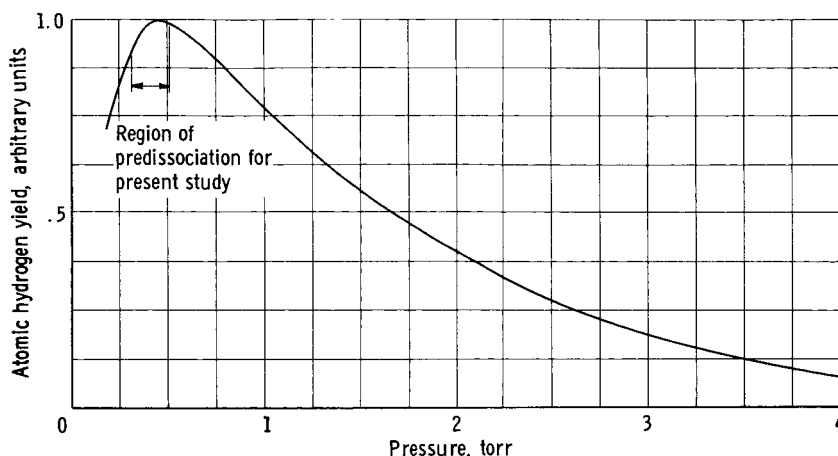


Figure 2. - Effect of pressure on atomic hydrogen yield (from ref. 5). For optimum conditions peak of curve equals 90-percent dissociation.

requirements include (1) a 9/16-inch-diameter discharge tube, (2) a gas flow rate of less than  $10^{-5}$  mole per second, and (3) a maximum of 200 watts of power dissipated in that plasma where dissociation occurs. The microwave generator used in the present work had a minimum power output much greater than 200 watts; therefore, a power divider was used which gave a net forward power range of 210 to 360 watts at the microwave cavity. The remainder of the power was dissipated into a dummy load. A link circuitry was used for coupling the radiofrequency power into the low-pressure hydrogen plasma. An equivalent network of this circuitry is shown in the inset in figure 1(a). Both the microwave generator and the radiofrequency generator were always operated under conditions of zero reflected power. Also, mirror magnets of 70 gauss and a faraday shield were used with the radiofrequency generator for a more stable plasma.

The effect of pressure on atomic hydrogen yield by a microwave generator, as determined in reference 5, is shown in figure 2. The predissociation of the present work was done near the maximum of this curve. In order to maintain a much higher pressure for producing atoms than that desired for ionization, an orifice was required. The proper orifice diameter at the desired pressure and flow rate was experimentally determined to be 0.04 inch. The orifice was made by grinding the proper size hole in the end of a quartz tube, and then an extension was added beyond the orifice so that a good vacuum connection could be made (fig. 1(b)). The dissociation was produced in the upstream end of the quartz tube as close to the orifice as possible.

The low-pressure side of the apparatus was constructed with heat-resistant glass pipe; the blank flanges were made of brass; and the vacuum seals were made with O-rings. Since glass is a noncatalyst for atom recombination, it is a desirable material of construction (ref. 11). Metal surfaces catalyze hydrogen atom recombination (ref. 15); therefore, these surfaces were covered with a noncatalytic plastic.

A 6-inch oil-diffusion pump with a liquid-nitrogen cold trap, which has a nominal

pumping speed of 700 liters per second and a pressure range of  $10^{-7}$  to  $5 \times 10^{-3}$  torr, provided the vacuum necessary for the tests. Cold cathode ionization gages and a McLeod gage were used to measure the pressures. The ionization gages were calibrated against the McLeod gage. Since there was no measurable pressure drop from the inlet to the exit of the low-pressure section of the apparatus, the test pressure measurements were made about 1 foot downstream of the radiofrequency coil (fig. 1(a)).

A differential catalytic probe (refs. 16 and 17) was used to indicate the presence of significant amounts of atomic hydrogen. More exact measurements were then made by using a 1.5-meter spectrograph. The differential catalytic probe measures the temperature differential between a catalyzing and a noncatalyzing surface; in these experiments, the difference amounted to  $7^{\circ}$  to  $10^{\circ}$  F. The spectrograph dispersion was 15 angstroms per millimeter. I-O 35-millimeter film was used for the spectrographic studies, because its high sensitivity over the wavelength of interest was desirable for the initial studies presented in this paper. Since high sensitivity also means large grain size, errors in line density measurements could be as large as  $\pm 25$  percent. (For the present studies, refined techniques, such as prefogging the emulsion, were not believed to be warranted.)

Commercial hydrogen, which was better than 99 percent pure, was the test gas. Since a slight amount of moisture is required for a high degree of dissociation (ref. 5), the gas was used without predrying. A high-vacuum, low-flow valve controlled the gas flow. A calibrated rotameter was used to make certain the gas flow did not exceed  $10^{-5}$  mole per second, which is important for obtaining a high degree of dissociation (ref. 5).

## PROCEDURE

The test conditions used for the work reported herein are listed in table I. Because the orifice between the dissociation section and the low-pressure plasma section was a fixed diameter, a given pressure in the dissociation section automatically fixed the test

TABLE I. - TEST CONDITIONS

Ionization pressure, $\mu$	3.2	4.2	4.7	5.1
Dissociation pressure, $\mu$	370	410	450	510
Gas flow rate, moles/sec	$< 10^{-5}$			
Radio frequency power output, W	313			
Plasma electron temperature, eV	22			
Microwave power output for dissociation, W	0, 210, 260, 310, 360			

pressure for ionization. Ionization test pressures (3.2, 4.2, 4.7, and 5.1  $\mu$ ) were selected so that the dissociation pressures were always near the peak dissociation (table I and fig. 2). For each setting of test pressure, measurements were made at each microwave power listed in table I.



TABLE II. - HYDROGEN  
SPECTRAL LINES USED  
IN THIS STUDY

Spectral line	Wavelength, Å
Molecular lines	
Singlet	4628.0
Singlet	4580.0
Triplet	4554.2
Atomic lines (Balmer series)	
H <sub>γ</sub>	4340.5
H <sub>δ</sub>	4101.7
H <sub>ε</sub>	3970.1
H <sub>ζ</sub>	3889.1
H <sub>η</sub>	3835.4
H <sub>θ</sub>	3797.9
H <sub>ι</sub>	3770.1
H <sub>κ</sub>	3750.2

Spectra of the low-pressure hydrogen plasma were taken between the last two turns of the radiofrequency coil (fig. 1). The lines studied in these spectra are listed in table II. These lines were selected because the emulsion sensitivity and gradient were constant over the wavelength range of interest. As many as five spectra at various exposure times were required for each set of conditions in order to obtain the necessary line density data. Line densities on the developed emulsion were measured with an automatic recording densitometer. The relation between line density on the emulsion and relative intensity was obtained by calibration of the emulsion in the usual manner (ref. 18). Since the sensitivity and the gradient of the I-0 emulsion were essentially constant over the wavelength of interest, only one calibration curve was required.

The procedure involved with the spectral line study is a rather tedious and time-consuming process; therefore, some preliminary qualitative measurements were made in order to be certain that the spectral line studies would

yield some positive results. First, the success of bleeding the dissociated gas into the low-pressure section was determined with the catalytic differential probe; this was followed by visual observation of spectra made with and without prior dissociation. This second step was done to determine if there was sufficient difference in the spectra to warrant the spectral line studies. Figure 3 shows that there was, indeed, a significant difference in the spectra. The Balmer lines in spectrum c (no prior dissociation) are much less dense than the lines in spectrum b (prior dissociation), the exposure time of spectrum b being only slightly longer than that of spectrum c. Even spectrum a (prior dissociation), with an exposure time much less than that of spectrum c, exhibits Balmer lines that are more dense than spectrum c.

The intensity ratios of the 4628- and 4580-angstrom singlet molecular spectral lines to the 4554-angstrom-triplet molecular spectral line were used to determine the electron

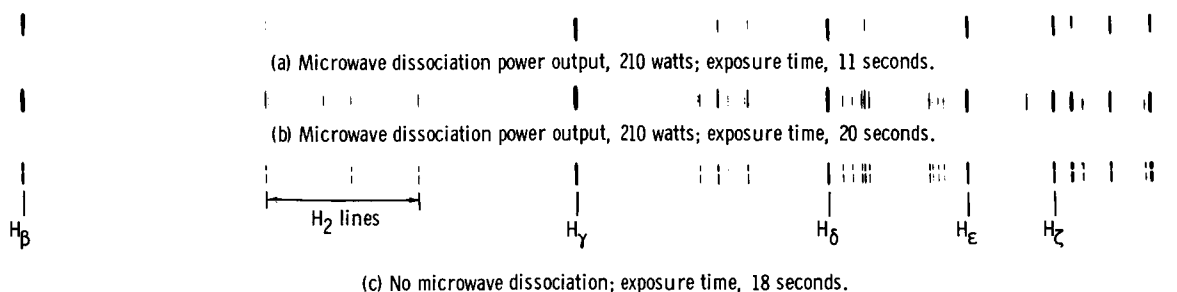


Figure 3. - Effect of prior dissociation on spectra of hydrogen plasma. Pressure, 3.2 microns.

energy of the low-pressure hydrogen plasma (refs. 19 and 20). These line intensity ratios showed that, over the test pressures of this study, the electron energy with and without predissociation was essentially constant. The electron energy, when a Maxwellian distribution was assumed, was  $22 \pm 3$  eV.

Spectra of the dissociation discharge were also taken. Visual observation of these spectra verified that the gas was highly dissociated. The most intense molecular lines were barely visible.

## RESULTS AND DISCUSSION

Measurements made with a 35-kilomegacycle-per-second microwave interferometer showed that for each of the test pressures the electron density in the radiofrequency region was not significantly affected by predissociation. Reflected power measurements in the radiofrequency circuit also showed that the electron density remained constant. A 5-percent change in forward power made a measurable change in the reflected power, but turning the predissociation discharge on and off did not affect the reflected power. The fact that predissociation does not change electron density significantly is in agreement with calculations made in reference 3. With both the electron energy and the electron density kept constant for tests at a given pressure, the percent increase in hydrogen ion production must equal the percent increase in atom concentration (eq. (2)).

Absolute atomic hydrogen concentration can be obtained with an electron paramagnetic resonance spectrometer (ref. 21). For the present work, however, conventional emission spectroscopic techniques were considered sufficient if a line produced only by the direct excitation of atomic hydrogen could be observed. Information on such a line is not available, but reference 22 does suggest that, for the Balmer lines, the contribution to the lines by excitations from molecular hydrogen decreases with decreasing wavelength. Hence, it was necessary to determine where this molecular contribution became insignificant.

The intensity of a Balmer line, which has no contribution from excitation of molecular hydrogen, is proportional to the atom concentration (eq. (5)). In logarithmic form, equation (5) becomes

$$\log I_{jk} - \log I'_{jk} = \log \frac{N_H}{N'_H} \quad (6)$$

Equation (6) holds for all the Balmer lines that arise only from direct excitation of atomic hydrogen. For all such spectral lines, the difference in the logarithm of the intensity is constant when the atom concentration ratio is fixed. A plot of log intensity against some

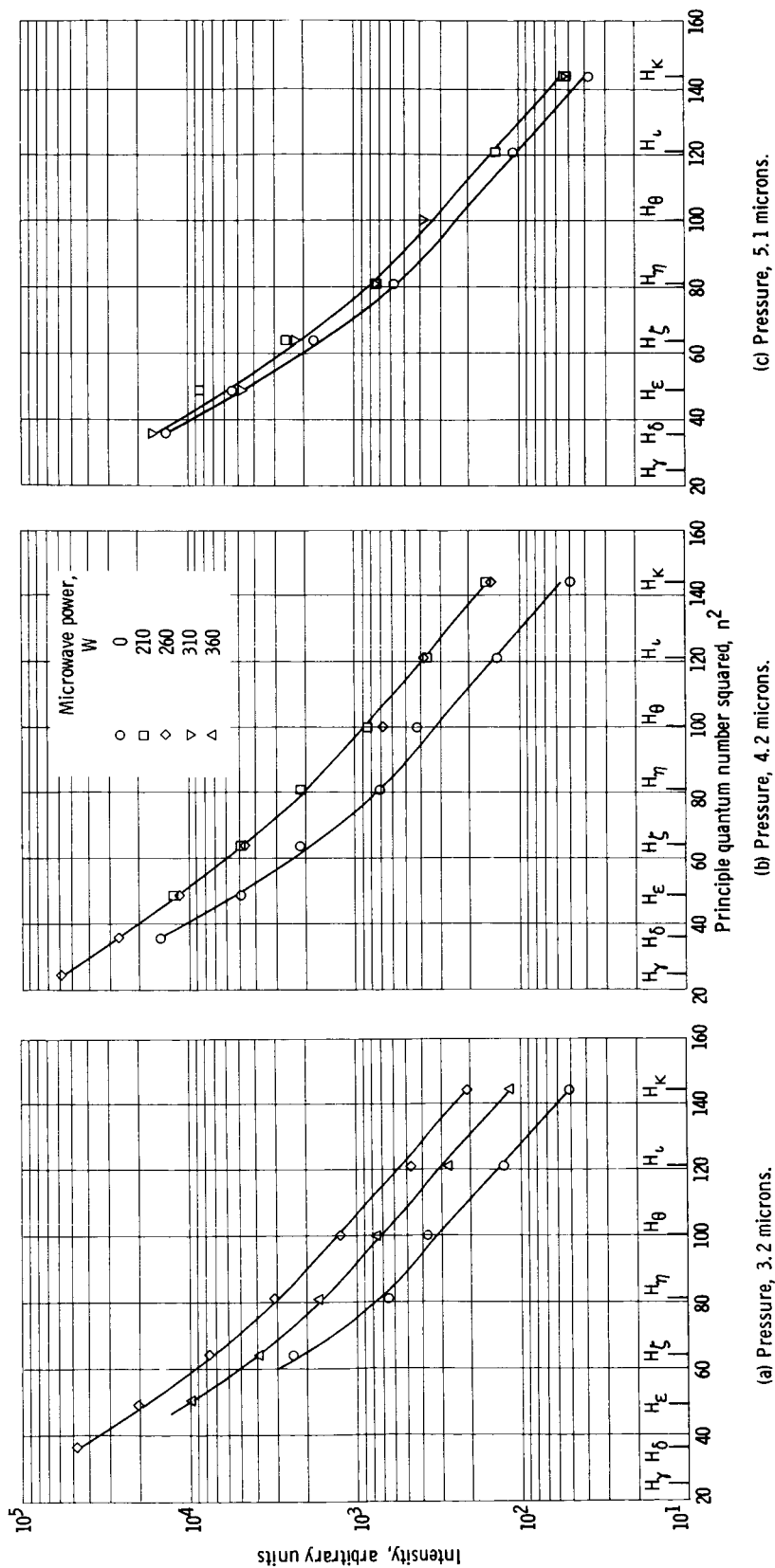


Figure 4. - Balmer line intensity of hydrogen plasma for various dissociation powers.

TABLE III. - INCREASE IN ATOMIC HYDROGEN  
CONCENTRATION OF TWO-STEP IONIZATION  
PROCESS OVER SINGLE-STAGE PROCESS

Ionization test pressure, $\mu$	Microwave dissociation power, W			
	210	260	310	360
	Increase in atomic hydrogen concentration, percent			
3.2	230	300	290	120
4.2	160	200	180	120
4.7	180	220	170	40
5.1	30	70	40	30

$H_K$  lines. For principle quantum numbers less than that of the  $H_\eta$  line, there is some molecular contribution to the lines.

Since the  $H_\eta$ ,  $H_\theta$ ,  $H_L$ , and  $H_K$  lines have little or no contribution from excitation of molecular hydrogen, these lines were used to determine the increase of atomic hydrogen caused by predissociation. Dividing the intensity of these lines at a given test pressure by the intensity of that same line without predissociation gives the increase in hydrogen ion production rate. Results are shown in table III. Atom concentration with no predissociation was estimated to be only about 5 percent. For each of the ionization test pressures, the maximum increase in atomic hydrogen always occurred at a dissociation power of 260 watts. When power losses to the apparatus and surroundings are considered, the results are in agreement with the 200-watt maximum dissipated power for maximum dissociation in reference 5. A maximum improvement of 300 percent, which means perhaps 15-percent dissociation, was observed when the ionization test pressure was 3.2 microns. The results show a general decrease in the improvement with increasing ionization test pressure. For microwave dissociation powers of 210 and 260 watts, this general downward trend is reversed at an ionization test pressure of 4.7 microns. The results behave in this manner because of competing processes: namely, (1) the variation in dissociation, which peaks at an ionization test pressure of 4.7 microns (dissociation pressure is  $450\mu$ , table I (p. 6) and fig. 2 (p. 5)); and (2) adsorption and surface recombination, which are increased with pressure.

Qualitative studies of spectra from both the microwave discharge and the  $H^+$  plasma indicate that atom recombination is taking place on the orifice walls. The grinding process used in making the orifice does tend to give a surface area much larger than that of fused glass, and hence, increases the catalytic recombination process. A glass-blowing process for making the orifice could eliminate this problem.

characteristic of the Balmer series will help identify these spectral lines. Figure 4 shows log intensity plotted against the square of the principal quantum number of the upper stage  $j$  of the transition. Since each curve in figure 4 is from a single spectrum, the atom concentration is a constant for each curve. Along the straight line portion of these curves, the difference in log intensity between two power levels is a constant and agrees with equation (6). The straight line portion of the curves in figure 4 includes the  $H_\eta$ ,  $H_\theta$ ,  $H_L$ , and

## CONCLUDING REMARKS

In the pressure range 3 to 6 microns, the atomic hydrogen concentration, and hence the rate of hydrogen ion production in a hydrogen plasma, can be increased by as much as 300 percent above that of a hydrogen plasma without prior dissociation. This increase can be accomplished by dissociating hydrogen under conditions conducive to dissociation prior to ionization. Surfaces exposed to the atomic hydrogen should be noncatalytic in order to keep surface recombination to a minimum. There was little or no contribution from molecular excitation to the  $H_{\eta}$ ,  $H_{\theta}$ ,  $H_{\iota}$ , and  $H_{\kappa}$  Balmer lines; therefore, the intensities of these Balmer lines were used to determine the effect of prior dissociation on the hydrogen ion production rate.

Lewis Research Center

National Aeronautics and Space Administration  
Cleveland, Ohio, April 30, 1965.

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